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A wet chemical sampling method using acidic absorbing solutions was used to determine levels of ammonia (NH_3) in syngas from a biomass gasifier. Before syngas is bubbled into the absorbing solutions, a quartz thimble filter is used to filter ash from the gas stream at 450 °C followed by heavy tar removal at about 100 °C. When gasifying corn, good precision was observed for multiple samples collected on any given day of testing. Tests on producer gas obtained from gasification of switchgrass revealed important conditions for successfully sampling NH_3. During gasification of switchgrass, high solids loading in the syngas caused the primary cyclone at the gasifier exit to plug, resulting in abnormally high ash loading in the thimble filter in the sampling system. While gasifying the switchgrass, the NH_3 levels showed a continuous decline throughout the day. It is suspected that NH_3 reacts with the ash in the thimble filter, confounding attempts to accurately measure NH_3 in the syngas.

Introduction

Gasification of biomass is a promising technology for producing hydrogen that could potentially be used in fuel cells. Alternatively, biomass gasification could be used to produce electricity by passing cleaned syngas into a turbine for power generation. Levels of trace contaminants in the syngas greatly impact end-use applications. Therefore, analyses for trace contaminants in the syngas produced during biomass gasification will be required to assess and optimize experimental gas cleanup methodologies, to provide chemical information on the syngas stream for feedstock evaluation, and to help assess gasifier performance. The amount of NH_3 in syngas from biomass gasification can typically range from 600 to 4000 ppm.[1] At those concentrations, NH_3 is of interest since it is a NO_x precursor. It has been reported that NH_3 and N_2 are the dominant species evolved from fuel nitrogen during biomass gasification, with lesser amounts of HCN.[2−4] The possible presence of small amounts of HNCO in gases from the pyrolysis of biomass has also been reported by some researchers.[5] The nitrogen content of the feedstock is the primary factor affecting NH_3 concentrations in the product gas,[6] although the structural formula of the fuel nitrogen also appears to affect the formation and evolution of nitrogen species during gasification.[2] The NH_3 levels generally decrease with increases in the freeboard temperature during gasification. However, actual NH_3 levels in syngas can vary widely, depending on the nitrogen content of the feedstock and the gasification process employed.[6]

Ammonia is commonly determined by using wet chemical sampling trains to absorb the NH_3, followed by off-line analysis of the absorbing solutions. The absorbing solutions typically consist of either dilute H_2SO_4 or HCl, and analyses of the absorbing solutions have been performed using techniques such as ion selective electrodes, colorimetry, and titration.[2,7] Instrumental techniques, such as FTIR, are also sometimes used for NH_3 analysis.[4,5,8] This paper provides a detailed discussion of an analytical procedure for off-line, wet-chemical determination of NH_3 in syngas from biomass gasification. Gasification feedstock materials for this work included seed corn and switchgrass.

Experimental Methods

Sampling System and Procedures. Maintaining sample integrity during sampling of syngas from biomass gasification is a critical prerequisite of the overall methodology for determining levels of NH_3 in the gases. The sampling system must either remove the heavy tars without losing NH_3, or else tar condensation must be avoided all together. Losses of NH_3

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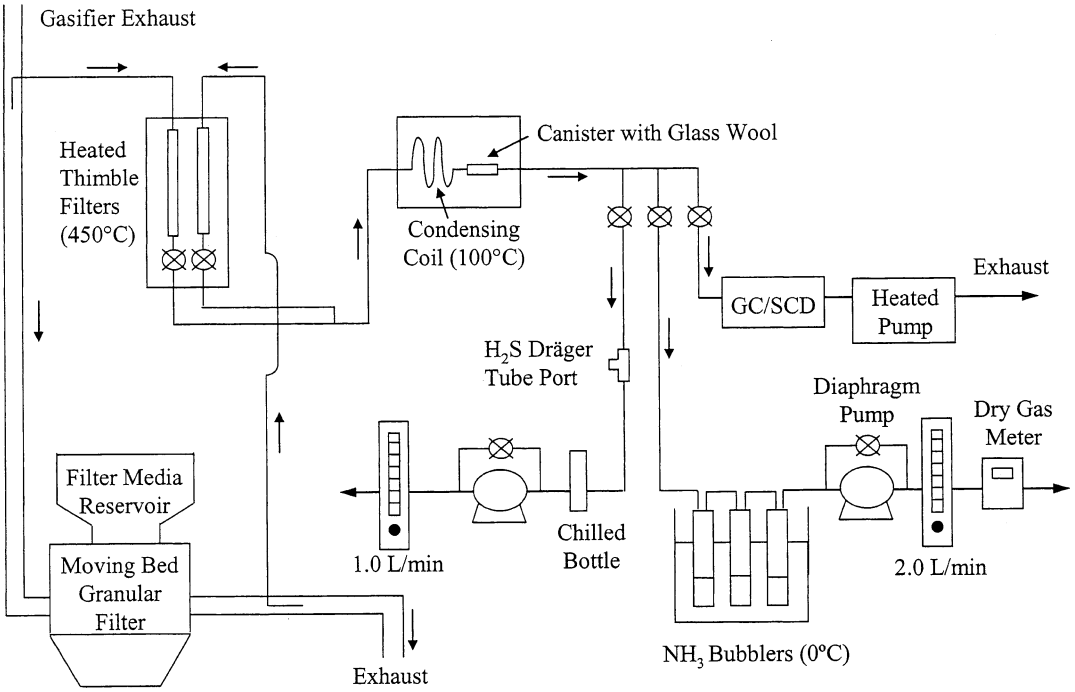

Figure 1. Schematic diagram of the trace contaminant sampling system.

resulting from interactions with components of the sample transport system (e.g., sorption onto the walls of the sampling lines) must also be avoided. In addition, since NH_3 is highly water soluble, condensation of moisture during sample transport cannot be allowed to occur. If moisture condensation occurs, a portion of the NH_3 will dissolve in the moisture and constitute a loss in some of the analyte. With these considerations in mind, an off-line, wet-chemical approach for the determination of NH_3 in syngas streams was developed. A schematic diagram of the overall trace contaminant sampling system installed on the gasifier is shown in Figure 1. In addition to sampling for NH_3, the system is set up for determining H_2S using Dräger tubes and for determining all gaseous sulfur vapors using GC with sulfur chemiluminescence detection (SCD). Details of the sampling system and the NH_3 sampling procedures are discussed below.

Syngas is drawn through the sampling system at a flow rate of about 2 L/min (STP) for about 15 min per sample. The sampling time may be adjusted, as needed, depending on levels of NH_3 anticipated to be in the gas stream. In this regard, the detection limit of the analytical methodology being employed must be considered. All sample lines upstream from the tar condenser are maintained at a temperature of 450 °C in order to prevent tar condensation. Particulate matter is removed from the gas stream by using a small (25 mm × 90 mm) quartz-fiber thimble filter in a custom-built steel assembly. The filter assembly is housed in an oven maintained at 450 °C. Prior to the installation of a thimble filter for ash removal, a large, highly porous, sintered metal filter had been used for ash filtration. Although 1000 ppm_v NH_3 (in nitrogen) could be quickly (within 10 min) transported through the system with negligible losses, the quartz thimble filter was used for ash removal for several reasons. First, the thimble filter was easier and less costly to maintain. Second, using the thimble filter dramatically decreased the surface area of the filter, thereby minimizing the potential for analyte losses on the wall surfaces. Finally, using the thimble filter allowed the gas stream to be filtered using a material (i.e., quartz) that is relatively nonreactive compared to steel. Although this is not a critical concern for NH_3, it is very important for the transport of other compounds (e.g., H_2S) that were being monitored.

After particulate matter was removed from the gas stream, the sample gases enter a tar condensation coil, which consists of 10−20 feet of 3/8 in. (9.5 mm) OD tubing. The condensation coil is housed in a modified home-style pressure cooker that is partially filled with water and heated to about 102 °C, which is above the moisture dew point of the gas stream. When the gases enter the tar condenser, the gas temperature quickly drops to about 102 °C. This allows the heavy tars to condense out in the coil while avoiding moisture condensation. Light hydrocarbons remain in the gas stream at this point but remain in the vapor phase. For our purposes, "heavy tar" does not refer to a particular chemical definition. Rather, the term is used only in a descriptive sense and refers to the hydrocarbons that are condensable at about 100 °C. Similarly, "light tars" are simply the hydrocarbons that do not rapidly condense at about 100 °C. The inner diameter of the tubing is sufficiently large to avoid plugging the coil with tar during sampling. In field tests, the coil could be used for 6 h or more before requiring cleaning with dichloromethane or other suitable solvent. Because tar aerosols are not always effectively removed by the coil, a canister containing glass wool is also housed in the pressure cooker and is attached to the exit of the condensation coil. This canister effectively removes the majority of heavy tar aerosols from the gas stream.

The particulate-free and (heavy) tar-free sample gases are then bubbled into a series of absorbing solutions to quantitatively collect the NH_3. For clarification, it should be noted that NH_3 rapidly dissolves in an aqueous system and forms NH_4^+ ion. Therefore, "NH_4^+" is the more correct term when discussing aqueous systems, while "NH_3" is the more correct term when discussing the gas phase (e.g., syngas). The sample line between the tar condenser and the impingers is heated to about 110 °C to ensure that no light hydrocarbons or moisture condense in the sample line. The impingers are maintained at about 0 °C by keeping them in an ice bath during sampling. Gases exiting the impinger system subsequently pass through a dry gas meter, which is used to measure the total volume of sample gas collected.

As noted above, sample gases are bubbled into a dilute acid solution to collect the NH_3. Although NH_3 would be soluble in the aqueous condensate that would form as the gas stream cools, condensation of the moisture and collection of the NH_3 in the condensate without an absorbing solution is undesirable since it can lead to reactions between trapped components. In addition, there is an increased risk of losing some of the NH_3

in that approach. Using an absorbing solution suppresses potential reactions between trapped components because they are dissolved in a large solution volume.[9] Because NH_3 is a basic compound, it is usually sampled with dilute acidic (e.g., H_2SO_4 or HCl) solutions,[9] which are very effective at capturing NH_3.

The current sampling protocol involves using a series of three precleaned 500-mL impingers. Modified (no tapered tip) Greenburg−Smith impingers are used since these are easier to clean. The first two impingers contain 200 mL of 5% (v/v) HCl absorbing solution, while the third impinger is filled with silica gel or other suitable desiccant. ACS reagent grade HCl and 18.0 MΩ deionized water are used to make the 5% HCl. The concentrated HCl used to make the 5% (v/v) HCl absorbing solutions has a maximum NH_4^+ concentration of 3 ppm_w, which means that the maximum NH_4^+ concentration in the 5% HCl will be less than 0.15 ppm_w. This is well below the 1 ppm_w detection limit for the titrimetric analysis being used. Although the current sampling protocol involves the use of HCl solutions to capture NH_3, we have also successfully used H_2SO_4 solutions for this purpose.

The sampling procedures have been continuously optimized in order to greatly reduce required personnel time, improve the efficiency of sampling operations, and minimize sample contamination potential. Recent improvements in the sampling protocol include using greaseless impingers, reducing the number of liquid impingers that need to be prepared and processed, decreasing the sampling time to only 10−20 min for raw syngas, and achieving a rapid analytical turnaround time of only a few days. This impinger-based method with the titrimetric analysis has an estimated overall uncertainty of ±5% on the basis of the analytical precision of the titrimetric procedure and on the basis of studies of NH_3 transport through the sampling system (see Sample Transport discussion in the Results section).

Sample Processing. After sampling syngas, the impinger solutions are immediately prepared for analysis and submitted to the analytical laboratory in precleaned 500-mL HDPE bottles. Since the analytical laboratory prefers 500 mL of sample for their distillation (required for the release of NH_3 during one of the sample processing steps) and titrimetric analysis, each impinger containing 200 mL of solution is processed separately. If the impinger solutions were combined rather than processed separately, there would not be adequate space in the sample bottles to hold the combined impinger solutions plus all the rinsings in a 500-mL bottle. Increasing the size of the sample bottles is undesirable since it would increase cost and slow the precleaning process.

After sampling raw syngas from the biomass gasifier, the impinger solutions are typically cloudy with a colloidal suspension. The colloidal material was analyzed by scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX) and was found to consist of oxygenated and sulfonated organic compounds with particle sizes of less than 0.2 μm in diameter. If the oxygen and sulfur were from the H_2SO_4, the amount of colloidal suspension could potentially be minimized by using HCl absorbing solutions. However, further tests showed that using HCl did not help avoid the colloidal suspension. Therefore, the impinger solutions were filtered within 30 min of sample collection.

Filtration was performed using Whatman No. 42 filters in a Buchner funnel coupled to an Erlenmeyer flask with a sidearm. A pump or water aspirator was hooked up to the Erlenmeyer flask to speed up the filtering process. After the solutions were filtered, the filter paper was thoroughly rinsed with several small aliquots of deionized water to ensure that small amounts of NH_4^+ were not retained by the filter paper. This step is generally not necessary when working with NH_3 concentrations typical of raw syngas from biomass gasification. However, it is a good precaution to take when working with low levels of NH_4^+ (e.g., <50 μg/mL) in solution.

The filtrate from each sample was quantitatively recovered and diluted to 500 mL with deionized water. The filtered solutions can show color, but they should never be cloudy. If cloudiness persists, there was probably a problem with the filtration, and it should be repeated. The solutions should be acidified to a pH of <1 (if needed) with H_2SO_4 and should be stored in a dark place at 2−5 °C prior to analysis.[9] However, when starting with 5% acid solutions, the solutions should seldom require acidification after sampling. This issue is more important if sampling is performed with solutions of lower acid strength. The solutions stabilized with H_2SO_4 should be stable for at least a month.

As a final point in the NH_3 sampling protocol, it should be pointed out that a series of two impingers containing only 100 mL of absorbing solution each may also effectively capture NH_3. If so, this would cut the sample processing time in half since the two impinger solutions and the rinses could then be combined into a single sample for analysis. This would reduce analytical costs as well. To help determine whether impingers containing 100 mL of absorbing solution could effectively capture NH_3, a series of tests were performed in the laboratory. In those tests, NH_3 was bubbled through three consecutive 500-mL impingers containing 100 mL of 5% HCl each. A compressed, certified gas cylinder containing 9.6% NH_3 was used, even though this greatly surpasses NH_3 concentrations in typical raw syngas streams. This high level of NH_3 was selected since there are some feedstock materials, such as chicken litter, where NH_3 levels in the syngas can be on the order of several percent. Thus, this concentration was selected to cover a worst-case scenario. The gases were bubbled into the absorbing solutions at 2.0 L/min (STP) for 5 min. This flow rate is comparable to the flow rate used during actual field sampling. After the 5-min sampling period, each impinger solution was analyzed. Results of the analyses showed that over 99% of the total NH_3 was captured in the first impinger. Therefore, this modified procedure appears to work well for NH_3 collection. However, validation of this modified method with actual syngas streams is desirable before implementing it as the standard procedure.

Sample Analysis. Samples were initially analyzed by ion chromatography (IC). However, the results from those analyses appeared to be erroneous for the particular sample matrix involved. Specifically, the analyses indicated that there was little or no NH_3 present in the gas stream, even though there should have been a substantial amount of NH_3 present. Because the sampling procedure was believed to be sound, attention turned to the analysis of the impinger solutions. A series of tests were performed in the laboratory to help determine the source of the error. In one series of tests, a series of liquid standards containing 1, 10, and 100 ppm_w NH_4^+ were prepared in 5% H_2SO_4 and submitted for IC analyses. A 5% acid solution was used because that is what is normally used in field sampling operations. No NH_4^+ could be detected in any sample, even though all of the concentrations used should have been easily detectable (the IC had a detection limit of roughly 0.1 ppm_w or less). This indicated a significant analytical problem for this particular sample matrix. Attempts were made to neutralize the sample (e.g., with NaOH), but cations associated with the neutralizing agents caused interference problems. The standards were sent to another analytical laboratory with IC capabilities, and they were also unable to detect any NH_4^+. Subsequent tests showed that changing the type of acid to HNO_3 did not make any difference in the results. Since a conductivity detector is used for the analysis, the analysts believe the analytical problem is due to excessive ions

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Table 1. Effect of Acid Strength on IC Results Obtained on a Variety of 10 ppm_w NH_4^+ Standards

acid strength of solution (%)	reported NH_4^+ concentration (ppm_w)	
	sample set 1	sample set 2
5	0	0
2	3.6	0
1	1.0	0.8
0.5	8.6	2.2
0.2	7.4	3.0
0.1	4.4	1.5

Table 2. Effect of Acid Strength on Results Obtained on a Variety of 50 ppm_w NH_4^+ Standards

acid strength of solution (%)	reported NH_4^+ concentration (ppm_w)		
	colorimetry	titration	ISE
0.025	46	48	39
0.5	50	49	32
5	50	49	46

in solution (from the acid), which in turn leads to a large ionic background that makes NH_4^+ detection very difficult at low levels.

Next, a series of 10 ppm_w NH_4^+ standards in H_2SO_4 solutions of varying acid concentration were submitted for IC analyses. For each acid strength, two sets of identical 10 ppm_w standards were prepared and submitted. These tests were performed to determine the effect of acid strength on the IC data. Results of those tests are shown in Table 1. As can be seen from the data, the acid strength had a strong effect on the analytical results. As noted above, the high ionic background associated with the concentrations of H_2SO_4 used for the sample matrix is probably responsible for the analytical difficulties.

Next, 50 ppm_w NH_4^+ standards in 0.02, 0.5, and 5.0% H_2SO_4 were submitted to three different laboratories for analysis. One laboratory performed the analysis by colorimetry, one by titration, and one by ion selective electrode (ISE). Results of those analyses are shown in Table 2. As can be seen from the data, excellent results were obtained using both the colorimetric and titrimetric analyses. For the ISE method, it is anticipated that the high ionic strength (due to H_2SO_4) of the solutions was causing errors in the analysis, as was probably the case for the analyses by IC. The titrimetric analysis was selected as the analytical method to be used for performing routine analyses on the impinger solutions. Also, the laboratory performing those analyses was located in close proximity to the gasification research facility, which facilitated submitting samples. If HNCO is present in the syngas, this can be trapped in the impinger solutions and converted to NH_3.[10,11] However, levels of HNCO in the syngas are expected to be very low and therefore should not lead to any NH_3 measurement errors. Results of the titrimetric analyses are used to calculate NH_3 concentrations in the syngas from the biomass gasifier. This is done by dividing the total amount (in micrograms) of NH_3 collected by the total volume of dry gas (at STP) sampled.

Sample Transport. It has been reported that sampling for NH_3 can be difficult since it reacts easily with surfaces of sampling systems, as well as with impurities in the gas stream.[9] Proper sampling of the gas stream is critical in order to obtain reliable data on the NH_3 levels present in the syngas. Therefore, tests were conducted to determine whether NH_3 could be successfully transported through the entire sampling system.

Initially, laboratory tests were performed using a gas stream containing 60 ppm_v NH_3 in a nitrogen balance. This gas stream was passed through a 56 cm (22 in.) section of 0.95 cm (3/8 in.) OD stainless steel tubing using a gas flow rate of 1 L/min (STP). The steel tubing was heated to temperatures of 25, 200, and 400 °C by using a tube furnace. The NH_3 concentration in the gases exiting the steel tubing was monitored continuously using a Zellweger Analytics Model 7100 continuous toxic gas monitor equipped with a NH_3 detection tape. These tests were performed to determine if steel components of the sampling system on the biomass gasifier react quickly with low levels of NH_3 to the point of being an issue of concern during sampling. If NH_3 interactions with the steel were a major problem, a significant effect on the 60 ppm_v NH_3 stream should be observed. For comparative purposes, identical tests were performed while using Teflon tubing at 25 and 200 °C (Teflon will melt at 400 °C, so tests with Teflon at that temperature were not performed).

A number of validation tests were also performed to check the transport of NH_3 through the entire sampling system installed on the biomass gasifier. For these tests, all components of the sampling system were heated to their normal operating temperatures. A gas blend containing 500 ppm_v NH_3 and 50 ppm_v H_2S in a nitrogen balance was used at a flow rate of 2 L/min (STP). The high-temperature ash filter and the condensation coil were both very dirty (with ash and tar, respectively) from an earlier gasification test with corn. The ash filter and tar condenser were not cleaned prior to testing in order to more closely simulate actual sampling conditions. Dräger tubes (colorimetric detection tubes) were used to determine the NH_3 concentration in the gases entering and exiting the sampling system.

Field Sampling. NH_3 concentrations in the raw syngas from an atmospheric, bubbling bed, fluidized-bed biomass gasifier were determined. A pilot-scale fluidized-bed reactor located at the Biomass Energy Conversion (BECON) facility in Nevada, Iowa was used. The gasifier is rated at 800 kW thermal input, which corresponds to an average throughput of 180 kg/hr of biomass having a heating value of about 16 300 J/g. For most of the gasification tests, seed corn from Pioneer Seed Company was used. In addition, a single day of testing was performed while gasifying switchgrass. Typical nitrogen contents for the corn and switchgrass are 1% and 0.5% (as-received bases), respectively. The syngas downstream from the NH_3 sampling location was periodically analyzed for oxygen with a Varian CP-2003 Micro-GC to determine whether the sampling system had any leaks. These tests were done prior to collecting the first NH_3 sample, as well as after all NH_3 samples had been collected. In all cases, there were no indications of any leaks. A summary of the gasification tests discussed in this paper is provided in Table 3. The gasifier bed temperatures are included in this table. It should also be noted that the freeboard temperatures were always within 10 °C of the bed temperatures.

For Test Series 1, the two samples (two acid impingers per sample) were collected back to back. In other words, when the first sampling was finished, the second sampling was started immediately. After sampling was completed, the second impinger solution from each of the sample sets was filtered and then split into two equal portions. One of those portions from the second impinger of each impinger set was spiked to increase the NH_4^+ concentration by 500 ppm_w. The spikes were performed to help determine whether there were any sample matrix effects that might interfere with the titrimetric determination of NH_3. On the basis of tests performed in the laboratory, the assumption was made that at least 98% of the NH_3 would be collected in the first impinger. Therefore, the second impinger solution in each impinger set should contain very little NH_3 (prior to spiking) but was still tinted from the presence of other gaseous components collected from the syngas stream. This is important in order to help assess possible matrix effects associated with the other gas stream components that are collected in the impinger solutions. All of the impinger solutions were then analyzed to determine the NH_3 content of the syngas stream. Specifically, the solutions

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Table 3. Summary of Biomass Gasification Tests

test series	feedstock	absorbing solution	number of samples[a]	duration of gasification (h)	temperature of bed (°C)
1	corn	5% H_2SO_4	2	4	735
2	corn	5% H_2SO_4 and HCl[b]	4	3	735
3	corn	5% HCl	4	3	790
4	switchgrass	5% HCl	4	4	735

[a] The number of samples (15−30 min each) collected over the duration of the gasification run. [b] Some of the samples in this test series were collected using H_2SO_4 impingers, and some samples were collected using HCl impingers for comparative purposes.

that were analyzed were (1) the first impinger solution in each impinger set, (2) the unspiked fraction of the second impinger in each impinger set, and (3) the spiked fraction of the second impinger in each impinger solution.

For Test Series 2, four samples (two acid impingers per sample) were collected over a period of 3 h. The samples (which lasted 15−30 min each) were spaced approximately evenly over the 3 h period. The first two samples used H_2SO_4 absorbing solutions, while the last two samples used HCl absorbing solutions. After sampling was completed, the first impinger solution from one of the impinger sets was split into two equal portions. One of the portions was filtered and analyzed as usual. The other portion was spiked *prior* to filtering to provide a concentration increase of 500 ppm_w NH_4^+. The spiked solution sat undisturbed for 24 h before the solution was filtered and submitted for analysis. The purpose of this test was to determine whether the colloidal suspension adsorbs significant amounts of the NH_4^+ in solution. Also, this served as an additional test on potential matrix effects.

Only HCl absorbing solutions were used in Test Series 3. However, the volume of the HCl solution in the impingers was varied. Specifically, the impingers contained either 100 mL or 200 mL of HCl. The first three samples were collected using 200 mL of absorbing solution in each liquid impinger (the normal procedure), while the fourth sample was collected while using only 100 mL of HCl in each of the two liquid impingers. The HCl volume was varied to help determine whether 100-mL impinger solutions would still effectively capture the NH_3 under field testing conditions. If so, then processing of the impinger solutions after sampling would be simplified because the contents of the two impingers could be combined and analyzed while still staying within the desired volume limit of 500 mL (including all rinses). If 200-mL solutions are used, combining the two impinger catches would often exceed 500 mL once the rinsings are added.

Results

Sample Transport. In the laboratory tests performed with 60 ppm_v NH_3 in nitrogen, results of the tests showed that the NH_3 could be easily transported through the stainless steel tubing at 25, 200, and 400 °C without any detectable losses. NH_3 concentrations downstream from the heated tubing reached steady levels within several minutes, at which point the NH_3 concentration at the inlet and outlet of the steel tubing were the same. The same results were obtained when using the Teflon tubing at 25 and 200 °C. Thus, it does not appear that contact with steel sample lines (and other steel components of the sampling system) in the temperature range of interest is a significant problem for transporting low levels of NH_3 at a gas flow rate of at least 1 L/min (STP).

In the tests performed with a nitrogen stream containing 500 ppm_v NH_3 and 50 ppm_v H_2S, the NH_3 transported through the heated sampling system very quickly, as determined by gas stream analysis using Dräger tubes. Based on the results from the Dräger tubes, the NH_3 reached its full concentration at the sampling port within about 5 min. These test results were also confirmed by bubbling the gases into acidic absorbing solutions and then analyzing the solutions for NH_4^+ content. Results of those solution analyses indicated that the amount of NH_3 collected at the sampling location was within 5% of the amount anticipated if no losses occurred. The anticipated amount of NH_3 was calculated on the basis of the NH_3 concentration in the gas stream, the measured gas flow rate, and the total sampling time. In addition, results from duplicate tests were within 0.5% (relative) of one another. Therefore, in a simple gas matrix, NH_3 was transported very effectively through the entire sampling system.

Field Sampling. *Test Series 1.* Results of the titrimetric analyses on the spiked impinger solutions showed that full (95−100%) recoveries of the spikes were obtained. Therefore, significant analytical matrix effects do not appear to be associated with the filtered solutions, even though the solutions are slightly or moderately colored. As expected, results of the analyses showed that 98% of the NH_3 was collected in the first impinger of each impinger set. This is in excellent agreement with results obtained in the laboratory when using synthetic blends of NH_3 and nitrogen. Results from the titrimetric analyses on the first set of impingers indicated that the NH_3 concentration in the raw syngas stream was 5540 μg/L. For the second set of impingers, results from the analyses indicated that the NH_3 concentration in the syngas was 5370 μg/L. The average and standard deviation are 5455 ± 120 μg/L, with a relative standard deviation (RSD) of only 2%. Thus, excellent repeatability was obtained for these sample sets, even under field conditions.

Test Series 2. Results of the impinger analyses showed that there was a 90% recovery of the 500 ppm_w NH_4^+ spike that was added to an unfiltered sample and allowed to stand undisturbed for 24 h. This shows that the colloidal suspension in the solution and the liquid matrix in general does not cause significant analytical uncertainties. Also, it should be pointed out that the impinger solutions are normally filtered within 30 min after sampling is completed. This further minimizes the potential for any reactions between the colloidal suspension and the NH_4^+ in solution.

The results from the four samples collected in this test series are shown in Table 4. Also, the results are shown in the same order that the samples were collected. The NH_3 concentration results from the HCl solutions were slightly higher than those from the H_2SO_4 solutions. On the basis of the averages obtained from the results with each acid (two samples each), the results obtained with HCl solutions were 15% higher than those from the H_2SO_4 solutions. However, one of the values obtained while using H_2SO_4 is significantly

Table 4. Results of NH_3 Determinations in Test Series 2

absorbing solution	NH_3 concentration in syngas (μg/L, at STP)
H_2SO_4, test 1	3720
H_2SO_4, test 2	3310
HCl, test 1	4120
HCl, test 2	3960

Table 5. Results of NH_3 Determinations in Test Series 3

solution volume (mL) per impinger	NH_3 concentration in syngas (μg/L at STP)
200	3640
200	3220
200	3320
100	3130

lower than the other values and appears to be an outlier. If that outlier were removed, then the results obtained while using HCl would only be 8% higher than the remaining value obtained while using H_2SO_4. It does not appear that the type of acid used affects results significantly. However, in view of the limited statistics, additional study is advised before a definitive conclusion can be drawn. If all four data points shown in the table are used, an average value of 3778 ± 352 μg/L NH_3 in the raw syngas is obtained. This gives an RSD of about 9%, which is good precision under field sampling conditions.

The NH_3 concentrations obtained with this test series are slightly lower than those obtained in Test Series 1. One of the variables that could explain the slightly different results between different sampling days while gasifying corn is that the tests conducted in Test Series 1 used a different dry gas meter than in Test Series 2 or 3. Therefore, gas meter calibration issues might come into play. Also, differences in NH_3 levels observed between different days of testing with corn might be related to operational parameters associated with the gasifier. As one example, even relatively small (e.g., 50 °C) changes in the gasifier temperature can dramatically affect the NH_3 levels in the syngas.[2] Possible variations in the nitrogen content of the corn could also be a contributing factor.

Test Series 3. The NH_3 results obtained from the impinger analyses are shown in Table 5. Results of the analyses showed once again that at least 98% of the total NH_3 collected was captured in the first acid impinger of each two-impinger set (even with the 100-mL solutions). The fact that nearly all of the NH_3 is collected in the first impinger is important because it suggests an approach for greatly reducing sample preparation time. If it is assumed that 98% of the NH_3 is always captured in the first impinger under a broad range of syngas compositions, and if a 2% loss is considered to be inconsequential, then only the solution in the first impinger needs to be routinely analyzed. This would cut sample processing time in half, reduce analytical costs, and reduce the time necessary to prepare impinger solutions for sampling.

Using 100-mL volumes of absorbing solutions seemed to give results comparable to those obtained when using 200-mL volumes, although definitive conclusions could not be drawn because of an apparent slight downward trend in the NH_3 levels with time. If only 100 mL of the absorbing solution are needed, then the two impinger catches can be combined to give quantitative recovery of NH_3 while greatly reducing sample processing time, impinger preparation time, and analytical costs.

Table 6. Results of NH_3 Determinations in Test Series 4

time (PM)	NH_3 concentration in syngas (μg/L at STP)
2:10	2190
4:10	1360
5:30	1320
6:00	816

The average NH_3 concentration was 3328 ± 222 μg/L. The RSD was less than 7%, which is excellent under field sampling conditions. As can be seen, the first data point for the NH_3 was slightly higher than the other data points. It is interesting to note that the H_2S concentrations (determined with Dräger tubes) also followed the same trend, with the first reading (taken at about the same time as the first NH_3 sample) being significantly higher than the subsequent readings taken periodically over a period of 3 h. Specifically, the H_2S values (in chronological order over a period of about 3 h) were 340, 230, 240, and 230 ppm_v. It is possible that the gas stream was still approaching steady state while collecting the first sample. However, additional work is needed to determine more conclusively the reason for the trend that was observed. If only the last three NH_3 data points are used, which is where the readings appear to have reached steady state, the average concentration is 3223 ± 95 μg/L. In that case, the RSD is only 3%.

Test Series 4. As noted earlier, Test Series 4 was the only set of tests involving gasification of switchgrass instead of corn. The NH_3 results from this series of tests are shown in Table 6. Because of the dramatic decrease in NH_3 concentration with time, the sampling times are noted in the table as well. As can be seen by the data for the raw producer gas, the NH_3 concentration decreased substantially with time. This trend is not normal.

During this particular series of tests, the primary cyclone on the gasifier was found to have plugged. Consequently, the ash content of the syngas stream was much higher than usual. Relative to normal ash loadings in the quartz thimble filter during a gasifier run, the ash loading was visually estimated to be at least 10 times the normal loadings over the sampling time frame involved. It is suspected that the NH_3 levels decreased as a direct result of the ash loading increasing with time. If increased ash loadings are indeed the reason for decreased NH_3 concentrations, it is not known whether the NH_3 is adsorbed on the ash or chemically reacting with it. The color of the impinger solutions was observed to become progressively lighter with each test, which is the first indicator that something atypical was occurring during sample collection. In previous gasification tests, there have been subtle suggestions that the NH_3 levels in the sample line were decreasing with time during normal ash loading conditions (see Table 5). This has important sampling implications because these results suggest that accurate NH_3 determinations will require low ash loadings in the filter. Lowering the temperature of the filter could potentially decrease the magnitude of any interactions occurring between the NH_3 and the ash, but we believe

Table 7. Summary of NH_3 Concentrations Determined in Raw Syngas from Biomass Gasification

		NH_3 concentration (μg/L at STP)		
test no.	feedstock	range	ave. $\pm$ σ	RSD (%)
1	corn	5374−5542	5458 ± 119	2
2	corn	3309−4117	3775 ± 351	9
3	corn	3132−3645	3330 ± 223	7
3[a]	corn	3132−3321	3226 ± 94	3
4	switchgrass	816−2191	1422 ± 569	40

[a] During this day of testing, the initial NH_3 concentration was significantly higher than the rest of the data. The data reported in this row were calculated *without* the initial data point that is somewhat anomalous.

it is best not to lower the filtration temperature in order to ensure that tars do not begin depositing on the filter (and possibly in the sample lines downstream from the filter as well). Additional work is needed to determine the impact of ash loading on the NH_3 results.

To simplify the comparison of data obtained for the different test series, a summary of the results obtained for the NH_3 concentrations in the raw syngas is presented in Table 7. Because of issues related to gas meter calibration, daily variations in gasifier operating conditions, and feedstock uniformity, caution should be used when comparing NH_3 data from the first set of tests with those from the other tests.

Discussion

As noted above, the results of our work showed that average NH_3 concentrations for a given test series ranged from roughly 3200 to 5500 μg/L when corn was used as the gasification feedstock. When gasifying switchgrass, the average NH_3 concentration was about 1400 μg/L. It has been reported that typical NH_3 concentrations in syngas from biomass gasification are in the range of 600−4000 ppm.[1] However, NH_3 concentrations outside of this range are not uncommon in view of the diversity in gasifier designs, gasifier operating conditions, and feedstock compositions.

NH_3 results from other studies vary greatly in view of the numerous variables involved. In one study, leucaena, sawdust, bagasse, and banagrass were gasified at different temperatures (ranging from 700 to 950 °C) in a bench-scale fluidized-bed gasification system.[2] NH_3 was found to be the primary nitrogen-containing contaminant gas derived from nitrogen in the fuel. The NH_3 concentrations in the syngas decreased dramatically as the temperature was increased from 700 °C to about 850 °C. As expected, the nitrogen content of the feedstock material also had a major impact on NH_3 levels in the syngas, with the NH_3 concentrations being directly proportional to the nitrogen levels in the feedstock. At gasification temperatures comparable to what was used in our study, NH_3 concentrations of 500−30 000 ppm_v were reported, depending primarily on the nitrogen content of the feedstock. In all cases, the nitrogen content of the biomass (which ranged from 0.3 to 2.5%) had a greater effect on NH_3 levels than the gasification temperature did.

In another study, almond shells and woody biomass were gasified at 850 °C in a downdraft, fixed-bed gasifier.[7] The NH_3 concentrations in the syngas were highly dependent on which feedstock material was being used and on the air-to-fuel ratio (gasification ratio), which varied from about 1.3 to 2.5. Depending on the feedstock and the gasification ratio, NH_3 concentrations ranged from 250 to 750 μg/L (at STP). The NH_3 concentrations increased as the gasification ratio was increased.

Other researchers gasified pine sawdust, pine bark, pine chips, forest residues, eucalyptus, and wheat straw in a pressurized, fluidized-bed gasifier operating with bed temperatures of roughly 900−1000 °C.[12] The nitrogen content of the feedstocks varied from 0.1 to 0.6% on dry basis (0.1−0.7% "as-received"). The NH_3 concentrations in the syngas ranged from roughly 300 to 2400 ppm_v (reported on a "wet gas" basis), depending on the feedstock and the gasifier conditions.

In yet another study, wheat straw and six woody-type feedstocks were gasified in an IGCC system.[4] The nitrogen content of the feedstock materials varied from 0.1 to 1.0%. Corresponding NH_3 concentrations in the syngas varied from about 400 to 4000 ppm_v and showed an excellent correlation with the nitrogen content of the feedstock material. For the wheat straw (which had a nitrogen concentration of 1.0%), the NH_3 concentrations in the syngas were about 4000 ppm_v.

Conclusions

NH_3 in syngas from a biomass gasifier can be effectively (without significant decomposition or losses) transported and subsequently sampled using a wet chemical sampling approach after first removing ash and heavy tars. In general, excellent reproducibility is observed for multiple samples collected sequentially over a period of several hours. Accumulated ash in the particulate filter upstream of the NH_3 collection solution is suspected of confounding NH_3 measurements. Although the effect needs additional investigation, periodic filter replacement can mitigate this potential problem.

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